APPLICATION NOTE

WATER ACTIVITY AND SHELF STABLE SEAFOOD

Seafood in its various forms is considered a delicacy by many around the world as well as serving as a food staple for many coastal regions. Unfortunately, fresh seafood is not shelf-stable due to its high water activity and long term storage requires either freezing or controlling the water activity through drying, smoking or salting. Shelf-stable seafood products are popular throughout the world and tend to be tailored to local flavors and fish supply. Water activity monitoring is critical if not mandatory to ensure the safety of shelf stable seafood products.

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SEAFOOD PRESERVATION

Drying is the most common method for creating shelf stable seafood and relies on lowering the water activity below the minimum growth limits for pathogenic bacteria by the removal of water (1). The next most common method of preservation is to lower the water activity through the addition of salt, often referred to as brining. Fish jerky and dried squid are examples of dried seafood products popular in parts of Asia while dried and salted cod fillets are examples of brined seafood products popular in Portugal and Italy (2). Some shelf stable fish products combine the effect of low pH through fermentation with water activity control through salting, such as the fermented fish sauce pla-ra in Southeast Asia (3).

Smoking is another common preservation method and while it will lower the water activity, it is more often monitored through a water phase salt determination (2).

Notice that for all the preservation methods listed above, water activity control is critical, but moisture content control is not mentioned. This is because preventing microbial growth depends on the water activity and not the moisture content. Water activity describes the energy state of water while moisture content measures the amount of water. Table 1 provides a survey of water activity and moisture content values for common shelf stable seafood products. Notice that products with nearly the same moisture content can have different water activity values while two products with very different amounts of water can have the same water activity. To understand why this is the case, let's define water activity and moisture content in more detail.

Product	Moisture Content (% d.b.)	Water Activity (a_w)
Mugil Dried Fish	28.4	0.71
Fufu Dried Fish	8.49	0.71
Fish Cracker	10.2	0.68
Dried Squid	12.1	0.56
Dried Catfish	37.3	0.78
Dried Anchovy	14.5	0.65

Table 1. Water activity survey of common types of shelf-stable seafood products (4)

WATER ACTIVITY AND MOISTURE CONTENT

Water activity is defined as the energy status of water in a system and is rooted in the fundamental laws of thermodynamics through Gibb's free energy equation. It represents the relative chemical potential energy of water as dictated by the surface, colligative, and capillary interactions in a matrix. As water interacts with other molecules through various interactions, a portion of the energy held in the bonds of the water molecule is transferred to the interaction, thereby lowering the energy of the water molecule itself. The more interactions provided to water through the addition of polar molecules such as salt, the lower the energy of water will become. This lowering of the energy of water also reduces its capability to escape into the vapor phase causing a reduction in vapor pressure.

Practically, a water activity test measures changes in the energy of water as reflected by changes in the partial vapor pressure of water in a headspace that is at equilibrium with a sample. As the energy of water is reduced, fewer water molecules have sufficient energy to escape into the vapor phase and contribute to the vapor pressure, resulting in a congruent reduction in the partial vapor pressure. This partial pressure is then divided by the saturated vapor pressure of water at the same temperature, creating a ratio from 0 to 1. A water activity of 0.50 indicates that the water in the product has 50% of the energy that pure water would have in the same situation. The lower the water activity, the less the water in the system behaves like pure water. Notice that the definition provided here never mentions the term 'free water' as this term is often mistakenly used to define water activity, but has no scientific meaning.

While water activity is an intensive property that provides the energy of the water in a system, moisture content is an extensive property that determines the amount of moisture in a product. Water activity and moisture content, while related, are not the same measurement. Moisture content is typically determined through loss-on-drying as the difference in weight between a wet and dried sample. For shelf stable seafood, moisture content provides a standard of identity and an expected mouthfeel but does not determine if the product is microbially safe. Referring to Table 1, the moisture content associated with a safe water activity will be different for each product and should never be relied on as an indicator of microbial safety.

WATER ACTIVITY MEASUREMENT

For shelf stable seafood, water activity is measured by equilibrating the liquid phase water in the sample with the vapor phase water in the headspace of a closed chamber and measuring the Equilibrium Relative Humidity (ERH) in the headspace using a sensor. The relative humidity can be determined using a resistive electrolytic sensor, a chilled mirror sensor, or a capacitive hyroscopic polymer sensor. Instruments from Novasina, like the Labmaster NEO, utilize an electrolytic sensor to determine the ERH. Changes in ERH are tracked by changes in the electrical resistance of the electrolyte sensor. The advantage of this approach is that it is very stable and resistant to inaccurate readings due to contamination, a particular weakness of the chilled mirror and capacitance sensors. The resistive electrolytic sensor can achieve the highest level of accuracy and precision with no maintenance and infrequent calibration.

WATER ACTIVITY AND MICROBIAL GROWTH

For shelf stable seafood, of greatest concern is the microbial safety of these products. They must be processed correctly to reduce the microbial load and prevent the subsequent proliferation of any microorganisms. Toxins produced by botulinum species, particularly Clostridium botulinum E, are particularly dangerous and must be prevented. Thankfully, the growth and toxin production by this organism is controlled at water activities less than 0.97 a_w. Consequently, it is recommended that even products targeted for control by refrigeration have a water activity less than 0.97 (5).

To understand why water activity controls microbial growth, let's begin with the basic understanding that each microorganism has an ideal water activity inside their cell and their ability to reproduce and grow depends on maintaining that water activity. When a microorganism encounters an environment where the water activity is lower than their internal water activity, they experience osmotic stress and begin to lose water to the environment as it moves to lower energy (1). This loss of water reduces turgor pressure and retards normal metabolic activity. To continue reproducing, the organism must lower its internal water activity below that of the environment so water will move back into the cell. It tries to achieve this by concentrating solutes internally. The ability to reduce its internal water activity using these strategies is unique to each organism. Consequently, each microorganism has a unique limiting water activity below which they cannot grow (6,7). Notice that an organism's ability to reproduce and grow does not depend on how much water is in its environment (moisture content or free water), only on the energy of the water (water activity) and whether it can access that water for growth.

A list of the water activity lower limits for growth for common spoilage organisms can be found in Table 2. Notice the growth limits for the various botulinum species important for seafood products. Notice also that all pathogenic bacteria stop growing at water activities less than 0.87 a_w while the growth of common spoilage yeasts and molds stops at 0.70 a_w, which is known as the practical limit. Only xerophilic and osmophilic organisms can grow below 0.70 a_w and all microbial growth stops at water activities less than 0.60. Other intrinsic factors such as pH impact microbial growth as well and water activity and pH can work synergistically to provide microbial protection at values higher than those required when only one control factor is considered (8).

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Microorganism	a_w limit
Clostridium botulinum E	0.97
Pseudomonas fluorescens	0.97
Escherichia coli	0.95
Clostridium perfringens	0.95
Salmonella spp.	0.95
Clostridium botulinum A B	0.94
Vibrio parahaemoliticus	0.94
Bacillus cereus	0.93
Rhizopus nigricans	0.93
Listeria monocytogenes	0.92
Bacillus subtilis	0.91
Staphylococcus aureus (anaerobic)	0.9
Saccharomyces cerevisiae	0.9
Candida	0.88
Staphylococcus aureus (aerobic)	0.86

Microorganism	a_w limit
Penicillum expansum	0.83
Penicillum islandicum	0.83
Debarymoces hansenii	0.83
Aspergillus fumigatus	0.82
Penicillum cyclopium	0.81
Saccharomyces bailii	0.8
Penicillum martensii	0.79
Aspergillus niger	0.77
Aspergillus ochraceous	0.77
Aspergillus restrictus	0.75
Aspergillus candidus	0.75
Eurotium chevalieri	0.71
Eurotium amstelodami	0.7
Zygosaccharomyces rouxii	0.62
Monascus bisporus	0.61

Table 2. Water activity lower limits for growth for common spoilage organisms.

GOVERNMENTAL GUIDANCE AND REGULATIONS

Due to their risk of being microbially unsafe, seafood products are typically regulated by governmental agencies. In the US, seafood products fall under the jurisdiction of the Office of Food Safety at the Food and Drug Administration (5). The Fish and Fishery Products Hazards and Controls Guidance document provides information on the most important hazards to consider for seafood products and gives guidance on establishing a Hazard Analysis and Critical Control Points (HACCP) plan (5). For each hazard, water activity control is identified as a critical control point and water activity monitoring is recommended to be a part of the HACCP plan. This is particularly true for shelf stable seafood products but as mentioned earlier, it is also recommended that even for refrigerated seafood products, the water activity should be below 0.97 to control botulinum E.

For a seafood product to be considered shelf stable, its water activity must be less than 0.86 a_w or its pH less than 4.6 to ensure that no pathogenic bacteria will be able to grow on the product. A shelf stable seafood product with a water activity higher than 0.70 a_w but less than 0.86 a_w is considered shelf stable but will still support the growth of mold and yeast. Shelf stable seafood in this range are not considered unsafe because the growth of molds and yeasts does not cause foodborne illness. However, the growth of non-pathogenic organisms does typically render the product undesirable to a consumer and is considered to have ended the shelf life of the product. Consequently, the water activity must be reduced to below 0.70 a_w or other interventions such as a preservative system or vacuum packing must be used to prevent mold growth.

THE MOST IMPORTANT SPECIFICATION

For shelf stable seafood, setting an ideal water activity specification is a critical step in formulating for safety and quality. The specification should be set to avoid microbial proliferation and ensure the safety of the product during storage. As mentioned earlier, the most common processing steps used to produce shelf stable seafood is to remove moisture through drying. However, shelf stable seafood products are typically sold on a weight basis, so removing water also reduces the weight of the product and results in lost revenue. Formulation adjustments such as salt levels can maximize the amount of moisture in a shelf stable seafood product at the water activity specification by reducing the amount of moisture that has to be removed. The amount of salt needed to reduce water activity to a desired level can be predicted using the Norrish and Ross equations and water activity application scientists can help setup a simple predictive tool to assist in formulation.

In addition, the careful monitoring of the water activity of shelf stable seafood during production can reduce energy inputs and prevent undesirable weight loss due to processing to lower than ideal water activities. This will reduce energy waste while maximizing revenue. In summary, establishing an ideal water activity specification, formulating to meet that specification, and monitoring production with frequent water activity testing will ensure a safe, quality product with an optimal shelf-life while maximizing revenue.

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